Smiljko Ašperger

Curriculum vitae

Professor Ašperger was born in Zagreb on January 25, 1921 to father Miroslav, attorney-at-law, (1887–1945) and mother Zora, née Petrović, (1893–1978). Smiljko had an older brother, Zdravko (1919–1997). Since his father's legal business did not go well in Zagreb, the family moved to Đakovo, the father's native town, in 1927. The Ašpergers were natives of Đakovo – they had come from Germany at the beginning of the 19th century – so the father hoped to establish a more successful law practice there. Smiljko started primary school in the same year when they settled in Đakovo and finished it in 1931. He attended and completed grammar school in Osijek (1931–1939). His older brother Zdravko went to grammar school in Sušak, studied medicine in Zagreb and became a well-known cardiologist. Smiljko studied chemical engineering in the Department of Chemical Engineering of the Technical Faculty in Zagreb from 1939 to 1943, when he graduated. He got his doctor's degree in 1946 by defending his doctoral thesis entitled *Kinetics of Photochemical Oxidations by Bichromate* at the same Faculty. His supervisor was Professor Karlo Weber (1902–1978). He habilitated in 1952 at the Faculty of Pharmacy and Biochemistry in Zagreb, where he worked until his retirement in 1986, first as a teaching assistant (1946–1952), then as a lecturer (1952–1958), associate (1958–1962) and full professor (1962–1986).

He was post-doctoral visitor at the University College in London (1954–1955) and University of Rochester, Rochester, N.Y., USA (1955–1957). During his part-time engagement with the Rugjer Bošković Institute (1958–1974), he founded the Laboratory for Chemical Kinetics and launched research in mass spectrometry. In this laboratory, he also initiated research in primary kinetic isotope effects of sulphur-34 and nitrogen-15 as well as research in secondary deuterium kinetic isotope effects. As visiting professor, he lectured to undergraduate and graduate students at several universities in the USA (1969–1970: seven months, University of Minnesota, Minneapolis; 1970: five months, Northwestern University, Evanston, Illinois; 1986: 5 months, Clarkson University, Postdam, New York; 1987: one month, Brown University, Providence, Rhode Island, *etc*.) and at many other universities worldwide. Professor Ašperger had a number of administrative duties at the Faculty of Pharmacy and Biochemistry. He was a dean in several terms (1959–1960, 1960–1962, 1964–1966, 1970–1972), chairman of the Faculty Council (1966–1968), head of the Chemistry Department (1970–1978), chair of Physical

Chemistry (1960–1986), head of the course »Physical Methods in Chemistry« within postgraduate studies in natural sciences of the University of Zagreb (1960–1986). The latter was one of the first postgraduate courses in Croatia. He also organized the first postgraduate course in chemistry at the Faculty of Chemical Engineering in Split (1963). He was also director of the Institute for Organic and Physical Chemistry of the University of Zagreb (1974–1975).

Jointly with Professor Marijan Pribanić, he published the textbook *Physical Chemistry* (Zagreb, 1962) and *Laboratory Exercises in Physical Chemistry* (Zagreb, 1968). He also participated in the translation of E. Wiberg's classical textbook *Inorganic Chemistry* (Zagreb, 1962, 1968). Professor Ašperger supervised 28 master theses and 17 doctoral theses.

Professor Ašperger took an active part in the activities of the Croatian Chemical Society. He was its President (1966–1968) and Vice-President (1968–1970) and a member of the Editorial Board of *Croatica Chemica Acta* (1959–1970). In 1998, he was elected an honorary member of the Croatian Chemical Society. In 1975, he became a candidate member of the Yugoslav Academy of Sciences and Arts (now the Croatian Academy of Sciences and Arts). He was elected associate member of the Academy in 1983 and its full member in 1991. He served as secretary of the Academy Department of Mathematical, Physical, Chemical and Technical Sciences (since 1998 – Department of Mathematical, Physical and Chemical Sciences) (1994–2000). He was awarded the state award for science »Rugjer Bošković« in 1967, the life-achievement award in 1992, and the Croatian Chemical Society's »Božo Težak« medal in 1996. He generously donated the entire amount of money given with the life-achievement award to the children of the Croatian soldiers fallen in the 1991–1995 liberation war.

Professor Ašperger's scientific contributions are mainly in the field of kinetics and reaction mechanisms of transition metal complexes, as well as substitution and elimination reactions of sulphonium and ammonium salts. In solving reaction mechanisms, he made use of the primary kinetic isotope effects of ^{34}S and ^{15}N and the secondary α- and β-deuterium kinetic isotope effects. He published a great number of research papers, all in the leading international journals.

His major achievements include the finding, which he made jointly with Karlo Weber, that the rate of glycerol and ethylene glycol photo-oxidation with dichromate decreases with increased temperature. This phenomenon enabled identification of the reaction mechanism that includes exothermic pre-equilibrium and reaction intermediates CrO_2 and Cr_2O_4 (*Nature* **157** (1946) 373; *J. Chem. Soc.* (1948) 2119). Chromium(IV) oxides had been unknown until then. He also established that UV light accelerates decomposition of hexacyanide into aquapentacyanide and solved the reaction mechanism

(*Trans. Faraday Soc.* **48** (1952) 617). He demonstrated that, analogously to UV light, catalytic activity is also manifested by Hg^{2+}-ions, since they participate in the transition state (*J. Chem. Soc.* (1953) 1041; *ibid.* (1955) 1449). He found that the catalytic activity of microquantities of Hg^{2+}-ions may be ideally followed in the presence of nitrosobenzene (violet complex). Methods for detection of mercury traces in the atmosphere, biological and inorganic materials were developed on this principle (*Anal. Chem.* **26** (1954) 543; *ibid.* **28** (1956) 1761; *ibid.* **31** (1959) 939, *ibid.* **33** (1961) 809). In collaboration with Sir Christopher Ingold (1893–1970), he developed a theory of the impact of orienting ligands, electron acceptors and donors upon the rate and stereochemistry of octahedral substitutions, which had an appreciable influence on later related studies (*J. Chem. Soc.* (1956) 2862). While working with Professor William H. Saunders Jr. in 1957, they discovered the secondary α-deuterium kinetic isotope effect (*Chem. Ind. (London)* (1957) 1417; *J. Am. Chem. Soc.* **80** (1958) 2421). This phenomenon was simultaneously and independently discovered by Andrew Streitwieser Jr. and his research group. The same phenomenon was also found by Professor Vladimir Prelog (1906–1998) and his co-workers (Stanko Borčić (1931–1994) and Kurt Mislow), whose work was published a little later but also in 1957. This effect was soon proven to be a powerful tool for solving organic reaction mechanisms. By means of the secondary α-deuterium kinetic isotope effect, Professor Ašperger revealed the structure of the transition state in solvolyses of ferrocenylmethyl esters. In formolysis and acetolysis, iron does not participate in the transition state and the conjugation with the π-system of pentadienyl predominates. Direct participation of iron in the transition state is not excluded in ethanolysis. In formolysis and acetolysis, quotients of Arrhenius' pre-exponential factors for the light and heavy isotopes amount to 0.38 and 0.49, respectively, allowing for the possible contribution of tunneling to the measured isotope effects (*J. Org. Chem.* **47** (1982) 5120; *J. Chem. Soc., Perkin Trans. 2* (1992) 275). He also prepared a new complex in the field of metalloporphyrins, Co^{III}-protoporphyrin IX dimethyl ester(metoxo)methanol, and demonstrated that the metoxo group, one of the strongest electron donors, stabilizes the metoxo intermediate, which therefore lives long enough to discriminate the entering ligands. As a result, the less alkaline amine ligands (4CN-py, 3CN-py, 3Cl-py, 4Cl-py, $pK_a < 4$, py = pyridine) bind in the transition state almost exclusively with the π-bond cobalt → ligand. In contrast, very alkaline ligands ($4NH_2$-py and $4(Me)_2N$-py, $pK_a \cong 9$) bind almost exclusively with the σ-bond. The same applies to imidazole derivatives as well. Here π-bonds include d_{xz} and d_{yz} cobalt orbitals whereas σ-bonds only the d_{z^2} orbital. In this way, an insight was obtained into the manner of ligand bonding in activated porphyrin complexes despite their short life span of only 5×10^{-13} seconds. This is of special interest because imidazole ligands, bound to the protoporphyrin macro-ligand,

play an important role in biology (*J. Chem. Soc., Dalton Trans.* (1985) 1095; *ibid.* (1991) 1847; *Inorg. Chem.* **35** (1996) 5232).

In 1999, the Croatian Academy of Sciences and Arts published his monograph *Chemical Kinetics and Inorganic Reaction Mechanisms*. The monograph won the Josip Juraj Strossmayer Award as the best book in the field of natural sciences, published in Croatia in 1999, jointly awarded by the Croatian Academy of Sciences and Arts and the Zagreb Fair.

Nenad Trinajstić